Elastic scattering of low-energy electrons by randomly oriented and aligned molecules
Influence of full non-spherical potentials

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Abstract

Elastic scattering of low (10–50 eV) kinetic energy electrons from free diatomic molecules is studied using a single-center expansion of the full molecular potential. Dynamic exchange and polarization are included in a local form. The calculated elastic differential scattering cross-sections (DCS) for electron impact on CO and N_2 are in good agreement with available experimental data. The importance of using the full molecular potential instead of a two-center potential approach is pointed out. These corrections are small for energies above 50 eV, but they become increasingly important at lower energies. When discussing the angular distributions of elastically-scattered electrons from oriented molecules (like surface adsorbates), we show that these corrections are particularly significant. The results have implications for other electron scattering problems such as those encountered in low-energy photoelectron diffraction from both core and valence levels. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Scattering of electrons from gaseous molecules is a classical problem of physics, of fundamental importance to many applied sciences, such as radiation physics or modeling of atmospheric and astro-physical systems, and has therefore attracted much experimental and theoretical interest. A large number of experiments for the low ($E \leq 50$ eV) energy range has been performed on a wide variety of systems from small to more complex molecules (see for instance Ref. [1] and references therein). The study of electron scattering from molecules typically refers to molecules with random orientations in a gas chamber, but there has been a growing interest in the last years in the study of scattering processes from

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oriented molecules, either aligned in space or adsorbed on surfaces both from the experimental [2] and the theoretical [3,4] point of view. The information that can be extracted from oriented-molecules scattering is by far richer as compared with the usual averaged information deduced from random molecules.

Several theoretical methods have been used in the study of low-energy electron scattering by molecules (for a review, see for example Ref. [5]), including multiple scattering models, the extensively used R-Matrix method and the Schwinger variational method, among others. In the methods based on a multiple-scattering approach of the incoming electron in the two centers of the molecule, the scatterers are usually represented by atomic spherical potentials truncated at suitable radii such that they do not overlap. Much effort has been dedicated to analyze within this multiple-scattering approach the shape of the local exchange and polarization potentials, comparing the theoretical results with experimental measurements and fitting (in some cases) the parameters describing the approximate form of the potential. However, such comparisons become problematic when the energy of the electron is low and non-spherical effects in the potential description become important.

In this work, we perform an expansion of the total molecular potential about a single center, reducing drastically the approximate character of previous multiple-scattering methods. We are thus able to perform parameter-free ab initio calculations of the total elastic differential cross-section and the angular distribution of the elastically scattered electrons. The intramolecular scattering is included in a single step calculating the total scattering matrix of the whole molecule. We point out the importance of these nonspherical corrections for the low energy range by comparing our full non-spherical potential method to the conventional multiple-scattering methods and to experimental data. We apply the formalism to the calculation of absolute elastic differential scattering cross-sections (DCS) and angular distributions of scattered electrons for electron impact on CO and N_2 and show good agreement with experimental data for low energies between 10 and 50 eV. We also emphasize the implication that this might have for other electron scattering problems such as those encoun-

tered in low-energy photoelectron diffraction from both core and valence levels [6].

Atomic units are used in the following, unless otherwise stated.

2. Theory

We want to describe the angular distribution of an initially parallel beam of electrons after crossing a gas of diatomic molecules. Only single-molecule collisions are considered (i.e. the gas is dilute enough to neglect scattering from more molecules). The static potential $V(\mathbf{r})$ that the external electron scatters off can be calculated as the sum of three different terms, the electrostatic potential $V_S(\mathbf{r})$, the exchange potential $V_{XC}(\mathbf{r})$ and the polarization potential $V_P(r)$:

$$V(\mathbf{r}) = V_S(\mathbf{r}) + V_{XC}(\mathbf{r}) + V_P(r) . \qquad (1)$$

Notice that only the latter term $V_P(r)$ can be approximated as spherically symmetric[1] . The other two terms strongly depend on the angle between the vector $\mathbf{r}$ and the axis of the molecule.

In our non-spherical full-potential approach, instead of using several centers to describe the electrostatic and exchange terms, we employ a single non-spherical potential. The total scattering potential is expanded in terms of spherical harmonics Y_L [the indices (l,m) are grouped in a single index L]:

$$V(\mathbf{r}) = \sum_L V_L(r)Y_L(\hat{\mathbf{r}}) , \qquad (2)$$

where $\hat{\mathbf{r}}$ is the solid angle of vector $\mathbf{r}$ in our system of coordinates, centered at the internuclear midpoint. The sum over L is truncated at a finite value $l = l_{max}$.

The electrostatic term of the potential is obtained by quantum-chemistry calculations of the ground state of the molecule, using the quantum chemistry program Gaussian [7] at Hartree–Fock level. The energy-dependent exchange potential is calculated using the Hara free-electron-gas approximation [8] from the electronic density of the molecule in its

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[1]The polarization potential $V_P(r)$ can be approximated as spherical in the center of mass of the molecule. As our choice of origin is the internuclear midpoint, $V_P(r)$ loses the spherical symmetry for heteronuclear molecules.

ground state. Finally, we include the adiabatic polarization potential described by Jain in Ref. [9]. Notice that our theoretical framework is parameter-free. Only the polarization potential can be considered as semi-empirical, but we do not fit any parameter during the calculation. Furthermore, we have checked that the exact form of the polarization potential plays only a minor role in the final value of the cross section, except for very low kinetic energies of the scattered electron.

When the potential does not have spherical symmetry, the scattering amplitude $f(\mathbf{k},\mathbf{k}')$ is given by [10]

$$f(\mathbf{k},\mathbf{k}') = -4\pi \sum_{L,L'} Y_L(\hat{\mathbf{k}}) \mathrm{T}_{LL'} Y^*_{L'}(\hat{\mathbf{k}}') , \qquad (3)$$

where $\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}'$ represent the direction of the electron before and after scattering, respectively, and the wavenumber $|\mathbf{k}| = |\mathbf{k}'|$. The coefficients $\mathrm{T}_{LL'}$ are the elements of the scattering T matrix in the partial-wave basis set and are calculated by numerically solving the Schrödinger equation (which is transformed into a system of coupled equations for non-spherical potentials) and imposing the appropriate asymptotic conditions at infinity [11,12]. An alternative procedure is the generalization of the Calogero variable-phase approach for a non-spherical potential, as described for instance in Ref. [13]. The differential cross section is directly obtained from the scattering amplitude [10] and has to be averaged over incident angles for randomly oriented molecules. The numerical calculation has been performed using the new EDAC code [14].

3. Results

The key point in our formalism is the expansion of the molecular potential in a single center [Eq. (1)] and the required truncation of the sum over L. Even if the Coulomb singularities of the molecular potential at the nuclei positions can not be reproduced by a finite sum, we have carefully checked that the calculation of the differential scattering cross section converges with the number of l's in the potential expansion (terms up to $l_{\max} \approx 15\text{–}20$ are typically needed), and that higher-l terms in the expansion only introduce negligible corrections to the cross-

section calculation. The latter convergence would be much more difficult to obtain for bound states, for which a very accurate description of the potential in the region close to the atomic nuclei is required. Of course, the convergence with the number of components in the T-matrix has also been checked ($l_{\max} \approx 6\text{–}15$) and found to scale approximately as $l_{\max} \approx kR$ (as it should, R being the range of the molecular potential). Vibrational effects can be neglected for our purposes: we have performed the same type of calculations modifying the internuclear distance by a factor of $\pm10\%$ and the results differ by less than 2%. The sensitivity of the scattering process to small variations in the potential has been tested using different descriptions of the exchange term $V_{\mathrm{XC}}(\mathbf{r})$ (all of them local): As expected, the energy-dependent Hara-exchange potential [8] produces better agreement with experimental data than a static Slater X-α exchange. The role of the polarization is much less important though.

We have compared the results that we have obtained with our full molecular potential (FMP) with two other models to gain insight into some of the problems that may arise when using approximations other than ours. The polarization potential remains constant in the three models and we calculate the electrostatic $V_{\mathrm{S}}(\mathbf{r})$ and exchange $V_{\mathrm{XC}}(\mathbf{r})$ terms in Eq. (1) in different ways. First, we have calculated $V_{\mathrm{S}}(\mathbf{r})$ and $V_{\mathrm{XC}}(\mathbf{r})$ as the sum of two spherical non-overlapping atomic potentials. As this is the usual scheme of calculations using the multiple-scattering formalism, we label this approximation MS, even if we do not follow this procedure. Second, we have calculated $V_{\mathrm{S}}(\mathbf{r})$ and $V_{\mathrm{XC}}(\mathbf{r})$ as the sum of two atomic potentials which, this time, we allow to overlap. We label this model AP (Atomic Potentials).

Our calculations show that the difference between the three models decreases when the kinetic energy of the electron increases and we have checked that it becomes negligible for kinetic energies of the order of 100 eV.

In Figs. 1 and 2, we compare our FMP calculations for the DCS of carbon monoxide at 15 and 50 eV with experimental data by Tanaka et al. [15] and Nickel et al. [16] and with the other two theoretical models explained above, MS and AP. In Figs. 3 and 4, our FMP calculations of the DCS for molecular nitrogen at 15 and 50 eV are compared with ex-
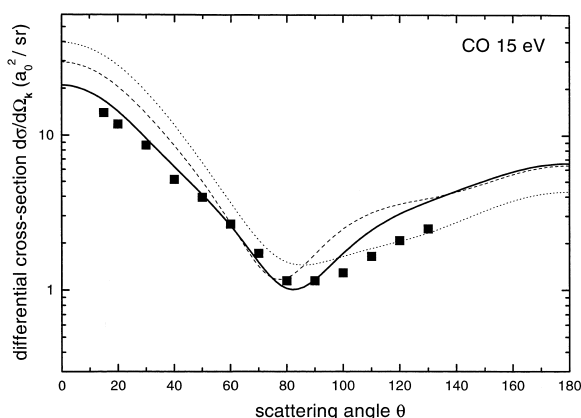
Fig. 1. Differential scattering cross-section for randomly oriented CO. The kinetic energy of the electron is $E_{kin} = 15$ eV. The solid line is calculated using the full-potential of the molecule (FMP), the dashed line corresponds to the sum of overlapping atomic potentials (AP) and the dotted line is calculated using two non-overlapping spherical atomic potentials (MS). Squares are experimental results by Tanaka et al. [15].

Fig. 3. Differential scattering cross-section for randomly oriented N_2. The kinetic energy of the electron is $E_{kin} = 15$ eV. The solid line is calculated using the full-potential of the molecule (FMP) and the dashed line corresponds to the sum of atomic potentials (AP). Squares are experimental results by Shyn et al. [17].

perimental data by Shyn et al. [17] and DuBois et al. [18]. We include AP results as well. Notice that the results are plotted in a logarithmic scale. Our FMP gives almost perfect agreement with experiment at 15 and 50 eV for both CO and N_2 at low scattering angles. For high scattering angles, our calculations tend to be slightly higher than the experimental data, a trend that becomes more significant with increasing electron energies. This discrepancy is usually found
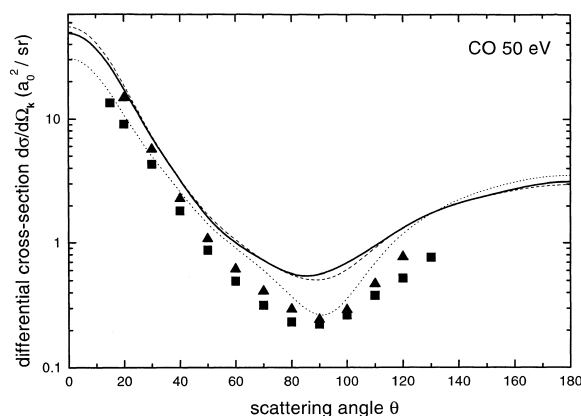
in any theoretical calculation in which absorption effects are not included (see Ref. [19] for instance).

Our comparison with the other two models emphasizes two different effects that are not included in a standard multiple-scattering model. The variation between the differential cross section in the FMP model and the AP model is due to purely molecular effects, i.e., to the rearrangement of the electronic

Fig. 2. Same as Fig. 1 but for $E_{kin} = 50$ eV. Squares are experimental measurements by Tanaka et al. [15] and triangles are experimental data by Nickel et al. [16].
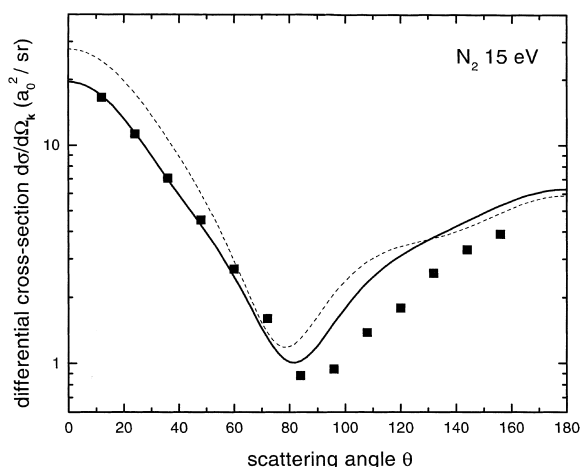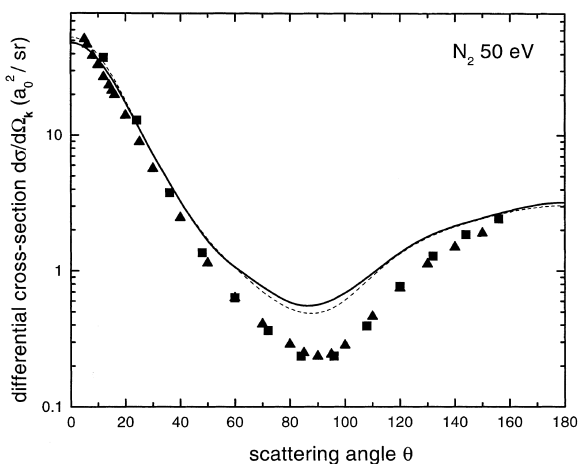

Fig. 4. Same as Fig. 3 but for $E_{kin} = 50$ eV. Squares are experimental measurements by Shyn et al. [17] and triangles are experimental data by DuBois et al. [18].

charge in the molecule when compared to the electronic structure of the isolated atoms. The MS model (equivalent to the conventional multiple-scattering-methods) is not only missing this molecular effect but also all information coming from the spatial region outside the non-overlapping spheres. Therefore, these calculations generally obtain poor quantitative results and may need to fit some of the potential parameters to experimental data.

The agreement between our results and the experimental data shows that a local treatment of exchange and polarization is good enough to repre-

sent the scattering in this range of energies (results are much worse for energies around 5 eV and less). Hence we can use our FMP model to confidently generate differential cross sections for CO molecules oriented in space. The results are shown for two different geometries and two different values of the electron kinetic energy in Figs. 5 and 6. The results obtained using the MS and AP models are plotted as well. Notice the slight asymmmetry (up and down) in the DCS in Fig. 6(a), due to the different scattering properties of the C and O atoms. Forward scattering along the incidence direction is dominant for any geometry when the energy is relatively high (50 eV).

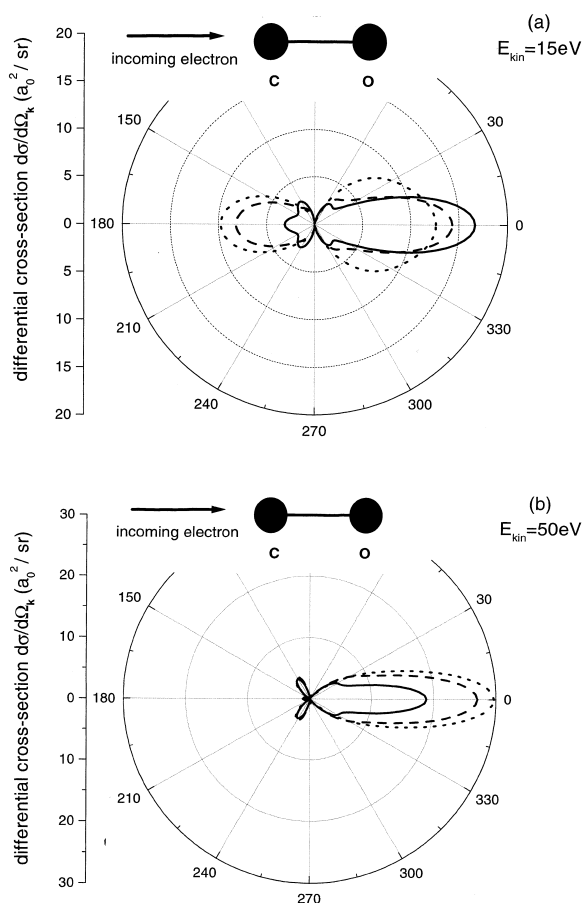The difference between the three theoretical models is much more important in these fixed-in-

Fig. 5. Polar plots of the differential scattering cross section for an aligned CO molecule. The geometry is shown in the Figure. The kinetic energy of the electron is $E_{kin} = 15$ eV in (a) and $E_{kin} = 50$ eV in (b). The solid line is calculated using the full-potential of the molecule (FMP), the dashed line corresponds to the sum of atomic potentials (AP) and the dotted line is calculated using two spherical non-overlapping atomic potentials (MS).
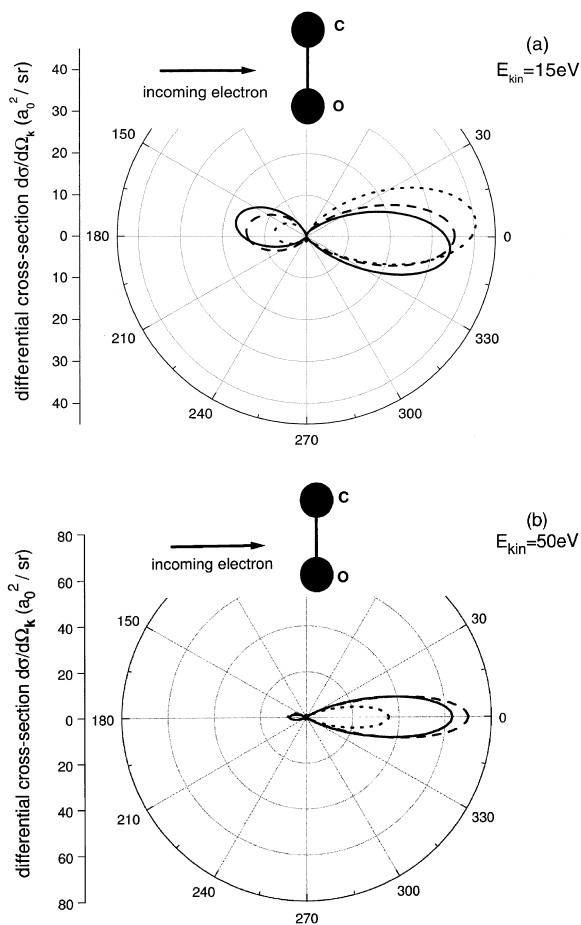
Fig. 6. Same as Fig. 5 but with the CO axis fixed perpendicular to the incident direction.

cident-angle geometries than it was for the randomly oriented molecules, in which these effects were smeared out by angular averaging. Figs. 5 and 6 are a clear example of the inaccuracy of the standard multiple scattering formalisms when calculating the continuum states of molecules in this energy range. This is particularly relevant when trying to describe the shape resonances of diatomic molecules, that have been the object of much attention in recent years, especially in photoemission experiments [20,21].

4. Discussion and conclusions

We have shown that a single-center expansion of the potential is able to reproduce all the features of the scattering for diatomic molecules. However, spherical potentials are able to reproduce only qualitatively the experimental DCS in elastic scattering calculations for low energies ($E \leq 50$ eV). The difference between the full molecular potential and the other two models used in this work may be a factor of two, both in the averaged DCS (as shown in Figs. 1 and 2, for instance) and in the DCS for fixed-in-space molecules (cfr. Figs. 5 and 6).

The calculations of the angular distributions of the scattered electrons for a given orientation of the molecule and a given electron incidence angle (Figs. 5 and 6) show the richness of the angular pattern structure and opens a perspective for new measurements and useful results at lower energies, either on aligned free molecules or on oriented molecules adsorbed on surfaces. The angular patterns of electrons with energies close to shape resonances should give as much information as the ones observed in photoionization [20–22], although the shape resonances would be of course different (the hole created by the incident light in the photoemission process is not present here).

Furthermore, theoretical work in progress on the angular distribution of photoelectrons in the photoionization of diatomic molecules [6] greatly benefits from our findings here. Multiple scattering between two centers (equivalent to our MS model potential) is one of the standard models used when describing photoemission from diatomic molecules [23,24]. We have shown that accurate calculations with a full

molecular potential very much improve this approximation. Multiple scattering between non-spherical scatterers is a natural solution to the problem [6] and is easily extended to larger systems (molecules, clusters and surfaces).

Acknowledgements

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